Trends in stratospheric and free tropospheric ozone

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Abstract. Current understanding of the long-term ozone trends is described. Of particular concern is an assessment of the quality of the available measurements, both ground and satellite based. Trends in total ozone have been calculated for the ground-based network and the combined data set from the solar backscatter ultraviolet (SBUV) instruments on Nimbus 7 and NOAA 11. At midlatitudes in the northern hemisphere the trends from 1979 to 1994 are significantly negative in all seasons and are larger in winter/spring (up to 7%/decade) than in summer/fall (about 3%/decade). Trends in the southern midlatitudes are also significantly negative in all seasons (3 to 6%/decade), but there is a smaller seasonal variation. In the tropics, trends are slightly negative and at the edge of being significant at the 95% confidence level: these tropical trends are sensitive to the low ozone amounts observed near the end of the record and allowance must also be made for the suspected drift in the satellite calibration. The bulk of the midlatitude loss in the ozone column has taken place at altitudes between 15 and 25 km. There is disagreement on the magnitude of the reduction, with the SAGE I/II record showing trends as large as -20 ± 8%/decade at 16-17 km and the ozonesondes indicating an average trend of -7 ± 3%/decade in the northern hemisphere. (All uncertainties given in this paper are two standard errors or 95% confidence limits unless stated otherwise). Recent ozone measurements are described for both Antarctica and the rest of the globe. The sulphate aerosol resulting from the eruption of Mount Pinatubo in 1991 and dynamic phenomena seem to have affected ozone levels, particularly at northern midlatitudes and in the Antarctic vortex. However, the record low values observed were partly caused by the long-term trends and the effect on the calculated trends was less than 1.5%/decade.

Introduction

Concern about the effect of man-made chemicals on the ozone in the stratosphere resulted in political action (the Montreal Protocol) to limit the use of chlorofluorocarbons (CFCs), halons, and a number of other gases. Over the last 10 years the scientific community has prepared a series of reports assessing our knowledge of ozone in the atmosphere (focusing on stratospheric ozone depletion) as requested by the Parties to the Montreal Protocol. These assessments have covered all relevant scientific aspects, from long-term trends in ozone, CFCs, and the other source gases, to the detailed chemical and physical processes which lead to ozone depletion. The latest was published in 1995. This paper reviews and summarizes our understanding of the trends in ozone discussed in chapter 1 of *World Meteorological Organisation/United Nations Environment Programme (WMO/UNEP)* [1995], in a manner similar to the review paper by *Stolarski et al.* [1992]. More recent work is also discussed.

It is relatively easy to detect ozone in the atmosphere. However, it has proved difficult to make sufficiently precise and numerous measurements to determine changes of a few percent in a decade. Difficulties include knowing how the absolute calibrations of the instruments change with time; assessing how much variability in any set of measurements is caused by the instrument and how much by the natural variability in the atmosphere; and interpreting comparisons of measurements made by different instruments, especially when different techniques are used. For detailed descriptions of the major techniques and instruments, see the *WMO* [1990a]; see also the following text for particular references.

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Ozone Measurement for Trend Analysis

Ground-Based Measurements

Uncertainties in the data are critically important in determining ozone trends of a few percent per decade and so have rightly been the subject of a great deal of scrutiny (e.g., *Bojkov et al.* [1988] for ground-based records). Data sets from a number of instruments have been used for the calculation of trends. Some of these measure both the total column of ozone in the atmosphere ("total ozone" is the amount of ozone integrated over the thickness of the atmosphere and is equal to on average, about 3 mm of ozone at STP) and how it is distributed with altitude. In this section we describe each instrument type separately, before considering the quality first of the measurements of total ozone and then of the vertical distribution of ozone.

Our knowledge of the long-term (pre-1979) variability in total ozone is derived from the measurements made by ground-based instruments, principally the Dobson spectrophotometer [e.g., *Bojkov and Fioletov*, 1995]. Some stations have continuous records going back to the late 1950s/early 1960s, and one station (Arosa, Switzerland) has a continuous record back to 1931. However, the geographic coverage was relatively poor until recently with an overwhelming preponderance of instruments in the northern midlatitudes and a few, luckily, in Antarctica.

The Dobson spectrophotometer measures the ratios of ultraviolet light at two pairs of wavelengths. Within each pair, one wavelength absorbs ozone strongly, the other weakly, so that the ozone absorption can be determined. The wavelengths were chosen to make the field measurements relatively simple and robust and to minimize the sensitivity to Rayleigh scattering and to extinction by stratospheric aerosols. The Dobson spectrophotometer can also be used to measure the ozone profile by means of the Umkehr technique [*Götz*, 1931; *Dobson*, 1968]. Measurements are made as the Sun is setting (or rising) and the vertical distribution of ozone inferred from the effect of the changing path of the sunlight through the atmosphere (in particular, as the mean altitude of the Rayleigh scattering changes).

The calibration of Dobson instruments has been maintained through a program of intercomparisons traceable to the international standard instrument (I-83) and through instrumental tests. The standard of maintenance of calibration has varied greatly from station to station, but the general quality has increased steadily over time [*WMO*, 1994]. The international standard has been calibrated since 1972 by a series of increasingly frequent trips to Mauna Loa, Hawaii, where the conditions for such measurements (clean atmosphere, high solar elevation at midday, etc.) are excellent. I-83 was first calibrated in Virginia, United States in 1962 and the U.S. station records are traceable to it from the 1960s. The stability of the international standard Dobson is estimated to be ± 1%/decade [*McPeters and Komhyr*, 1991].

The other ground-based instrument with a long record of total ozone measurements is the filter ozonometer (M83, M-124) which has been used in the network of the former Soviet Union (a large and important fraction of the northern middle to high latitudes) since around 1972. It works on a similar principle to the Dobson spectrophotometer but uses optical filters rather than quartz prisms to resolve spectrally. The filter ozonometer is less accurate than the Dobson spectrophotometer, but regional averages produce consistent ozone data sets [*Bojkov et al.*, 1994].

Vertical profiles of ozone have been measured since the 1960s by ozonesondes, lightweight electrochemical cells carried on small balloons to altitudes above 30 km. Several versions exist, based on the same principle, but with significant differences. The main instrumental problems stem from the fact that a different sensor is prepared for each profile measured. Quality control in both manufacture and preflight preparation is thus critical with changes in either capable of inducing long-term trends in ozone amounts. A number of inter-comparisons and other tests indicate that the quality of measurement is good in the stratosphere but not so good in the troposphere. In particular, there is an apparent discrepancy in the troposphere response of the two main types of ozonesonde (Brewer-Mast and ECC) used in Europe and North America whose cause is currently unresolved [*Kerr et al.*, 1994, and references therein]. It is thus hard to compare measurements made in the troposphere with the different sondes at different times. The geographic coverage is poor, with few long records with high launch frequency in the northern hemisphere and none in the southern.

Satellite Measurements

Near-global coverage arrived only with the introduction of satellite instruments. The backscatter ultraviolet spectrometer (BUV) operated for 1.5 years from 1970 and intermittently for an additional 2 years. Continuous measurement of ozone using satellites started in late 1978 with the launch of the Nimbus 7 satellite which carried two instruments that have produced long time series.

The solar backscatter ultraviolet spectrometer (SBUV) measures ozone by observing the amount of solar radiation scattered back from the atmosphere at 12 wavelengths between 255 and 340 nm. Judicious choice of wavelengths where ozone absorbs and does not absorb allows the calculation of both the total column and the vertical profile of ozone, although the profile is determined only at altitudes above the maximum concentration of ozone (about 25 km). The vertical ozone distribution is measured at low resolution (5-15 km, altitude dependent), while the horizontal resolution is quite high. SBUV operated from launch until June 1990. Improved instruments (SBUV/2) have been launched on the operational NOAA satellites and there is a near-continuous record of SBUV measurements since 1979.

The total ozone mapping spectrometer (TOMS) measures total ozone using the same technique as SBUV. TOMS uses fewer wavelengths than SBUV and does not measure the vertical distribution of ozone. It scans from side to side about the orbital track and so obtains greater horizontal resolution than SBUV which is nadir viewing. The Nimbus 7 TOMS made measurements until early May 1993. A revised version (version 7) of the TOMS data set was released in early 1996. Unless explicitly stated, we discuss only the version 6 data set here. A second TOMS was launched on the Russian Meteor 3 satellite in August 1991 and this instrument worked until December 1994.

The Stratospheric Aerosol and Gas Experiment (SAGE) measures the vertical profile of ozone at sunrise and sunset by solar occultation [*Chu et al.*, 1989; *McCormick et al.*, 1992].

The ozone absorption at 600 nm is measured and correction is made for molecular and aerosol scattering and NO_2 absorption. The vertical resolution is high (1 km), while the horizontal resolution is low. Two instruments have flown. SAGE I made measurements from February 1979 to November 1981. SAGE II started in October 1984 and continues to work. The SAGE I and II instruments are different in some respects, but in principle there are few reasons for calibration differences between them. There is a known offset in the altitude measurement of the two instruments. The largest effects on the inferred ozone trends are where the ozone concentrations vary most rapidly with altitude, which is between 15 and 20 km. The other main concern with the SAGE ozone measurements is whether the stratospheric aerosol correction is made correctly. In the trend analyses presented here, no SAGE data with aerosol extinction greater than 0.001 km^{-1} were used. Consequently, there are gaps in the SAGE ozone time series following major eruptions, whose length depends on altitude and latitude. For instance, using this criterion, SAGE II measurements were interrupted for 1 year after the eruption of Mount Pinatubo at 22 km near 40°S and 40°N and for 2 years at this altitude at the equator.

Assessment of Data Quality

Total ozone. Measurements made by the instruments described above are used in the trend analyses described in this paper. In this section we discuss the quality of the various measurement sets. A more detailed assessment can be found in *WMO/UNEP* [1995] and its predecessors, particularly in [*WMO/UNEP*, 1990a].

Over the past few years, two main data sets have been used for the determination of trends in total ozone: that from the ground-based Dobson network and that from the TOMS. As mentioned above, the calibration of the international standard Dobson instrument I-83 is estimated to be stable to ±1%/decade [*McPeters and Komhyr*, 1991]. The quality of the Dobson record has improved over the last 10 years, partly through retrospective reanalyses and partly through efforts to improve the quality of the measurements as they are made, e.g., the WMO traveling lamp program [*WMO*, 1992b; WMO/UNEP Report no. 35, in preparation]. The total ozone records from the filter ozonometer network in the territory of the former USSR have been revised using similar quality control procedures to those used for the Dobson measurements [*Bojkov et al.*, 1994]. The calibration of the filter ozonometers is performed using a Dobson instrument operated by the Main Geophysical Observatory in St. Petersburg.

One of the main tools used to assess the quality of the ground-based total ozone measurements since 1979 is the direct comparison of the ground-based measurement with the closest TOMS measurement, a so-called "overpass." Any changes in the difference between the measurements which are seen only at one ground-based station can be attributed to a change in the ground-based instrument. On the other hand, any changes seen at many ground-based stations can usually be attributed to a change in behavior of TOMS (see below). This use of the TOMS measurements as a check of the quality of the ground-based measurements has proved a very powerful tool.

It should be noted, however, that even though the TOMS data are used to identify possible problems and are not used to correct the ground-based measurements and vice versa (the quantitative corrections come from the instrumental calibration histories), the two data sets do lose some of their independence. The benefit of the improved understanding of the instruments and their uncertainties, which comes from careful inter-comparisons, more than offsets the loss of no longer having completely independent systems.

The measurements made when I-83 has been in Mauna Loa have been an invaluable test of the quality of the TOMS measurements, as direct comparisons can be made between the Dobson measurement and the closest TOMS measurements, the "overpass" [*McPeters and Komhyr*, 1991]. Figure 1 shows the overpass comparison (TOMS - Dobson) for I-83 at Mauna Loa (solid circles), as well as for those for I-83 at Boulder (open circles) and a set of 30 northern hemisphere Dobson stations (solid line; summer values, squares). Clearly, the TOMS and I-83 data at Mauna Loa are in very good agreement. The 4% offset is largely caused by a prelaunch calibration error of the TOMS instrument and is much smaller in the TOMS version 7 data.

The agreement between TOMS and Dobson instruments at midlatitudes is less good, as shown in Figure 1. From 1979 to 1993 the instruments drifted by 2-4%, and a seasonal cycle of about 2% (peak to trough) appeared. This behavior is seen in comparison with the Dobson network (as noted previously) and also in comparison with I-83 when it was at Boulder (the large error bars there arise from the relatively small number of measurements made). This evidence points to it being a problem with the TOMS data. The drift and its seasonal dependence are smaller in the TOMS version 7 data. The other major changes in the TOMS version 7 data result from the use of real cloud data rather than climatology, allowance for partially clouded scenes, an improved radiation transfer algorithm and correction for errors at high solar zenith angles [*Wellemeyer et al.*, 1993].

These problems, together with the facts that the Nimbus 7 TOMS instrument stopped working in 1993 and that the Meteor 3 TOMS instrument was in a precessing orbit, required

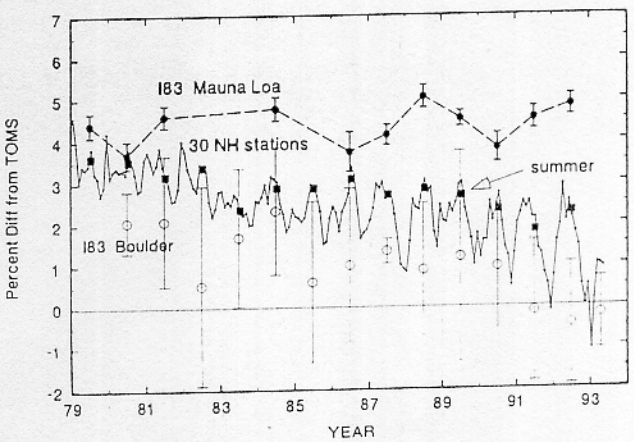

Figure 1. Percent difference in total ozone measured by the Total Ozone Mapping Spectrometer (TOMS) and the World Standard Dobson (I-83), at Mauna Loa (solid circles); I-83 at Boulder (open circles); and a network of 30 northern hemisphere Dobson stations (monthly average difference shown with dots; and summer only (JJA) differences shown in squares). The uncertainties shown are 95% confidence limits for the mean value.

a more careful examination of whether the SBUV data set was the more suitable. As noted above, measurements from the Nimbus 7 SBUV have to be combined with those from the improved instruments (SBUV/2) carried out on the operational NOAA satellites, in this case NOAA 11. The combined record is denoted SBUV(/2). There was an 18-month period of overlap in which the two instruments were in good agreement. Figure 2 shows the difference between coincident SBUV(/2) and TOMS measurements. The SBUV(/2) and TOMS records are stable from 1979 to 1989 or so, after which there is a drift of 1-2%. The seasonal cycle in the differences is probably caused by changes in TOMS. A comparison of the NOAA 11 SBUV/2 with an ensemble of ground-based stations between 20° and 60°N shows little drift from 1989 to 1994 and a seasonal cycle of 1-2% (minimum to maximum) whose cause is undetermined.

Taking all these factors into account, the better satellite data set for trend determination was judged to be SBUV(/2). One problem with the SBUV(/2) record is that the orbit of the NOAA 11 satellite drifted so that it measured away from local noon. Given the limitations of backscatter measurements at high solar zenith angles, the latitude range over which trends can be reliably assessed is at most 60°S-60°N year-round.

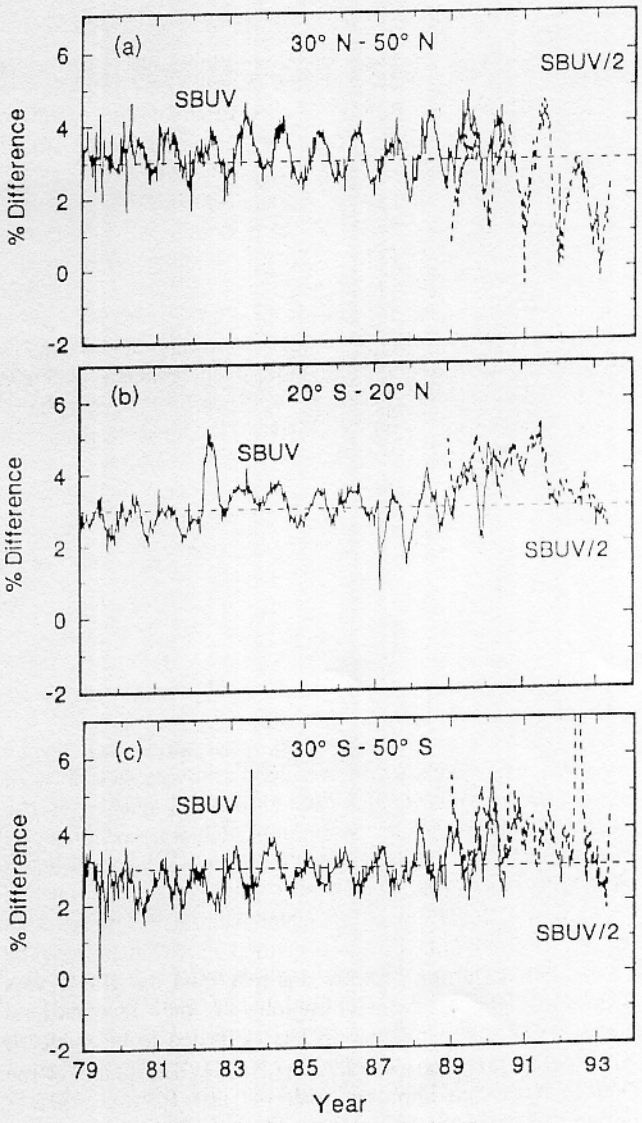

Figure 2. Weekly average differences in total ozone measured between by TOMS and the Solar Backscatter Ultraviolet instruments on the Nimbus 7 and NOAA 11 satellites (SBUV(/2)).

Vertical ozone distribution. It is much harder to evaluate the quality of the measurements of the vertical distribution of ozone than those of total ozone. Long-term measurements of the vertical distribution of ozone (using ozonesondes and the Umkehr technique) have only been made at a very few sites and so it is very hard to make a meaningful comparison of the data from nearby sites, as was done with the Dobson instruments. Since 1979, the SAGE and SBUV instruments have produced near-global measurements but certainly not with high spatial resolution on a daily basis. In this sense, TOMS, which does have daily, high spatial resolution, global coverage of total ozone is unique. Such coverage is necessary to make comparisons of the quality described above for total ozone. With fewer measurements from both the ground and space, the number of overpasses is greatly reduced. Nevertheless some comparisons have been made.

McPeters et al. [1994] have compared the SAGE II and SBUV measurements from 1984 to 1990. Collocated data were sorted into three latitude bands (20°S-20°N, 30°-50°S, and 30°-50°N). Agreement was found to be typically better than 5%. The main exceptions were near and below 20 km, where the SBUV ozone amount is not uniquely determined because it depends on the shape of the profile within its retrieved layers, and above 50 km where the diurnal variation of ozone was not accounted for in the comparison. At pressures lower than 32 mbar the (SBUV - SAGE II) drift from 1984 to 1990 is less than 5% and is statistically insignificant. At higher pressures the drift is 10% in the tropics and 4 to 6% at midlatitudes. Comparison of SAGE II measurements with those from near-coincident balloon and rocket measurements have shown agreement on average to within ±5-10% [*Attmanspacher et al.*, 1989; *Chu et al.*, 1989; *Cunnold et al.*, 1989; *De Muer et al.*, 1990; *Barnes et al.*, 1991].

Wang et al. [1996] compared the ozone profiles measured by SAGE I and SAGE II, in particular the altitudes of the SAGE I and SAGE II ozone maxima and the differing ozone amounts above the maximum when compared to SBUV measurements. They suggested that the error in the altitude determination of SAGE I is latitude dependent, being about 200 m in the tropics and about 400 m in the mid-latitudes. Wang et al. adjusted the SAGE I record according to their derived altitude adjustments and they further screened for aerosol interference in the SAGE II ozone measurements and omitted some January data. It should be noted that while this adjustment is an empirical one and is not based on 'internal' SAGE I data, it is consistent with the unknown offset (mentioned above) which was independently estimated to be 300 m [*WMO/UNEP*, 1995].

The different types of ozonesondes have been periodically monitored through a series of inter-comparisons [*Kerr et al.*, 1994, and references therein]. The measurements in the stratosphere were found to be in consistently good agreement. In the most recent WMO campaign (1991) the Brewer-Mast sonde gave results 15% higher than the ECC in

the troposphere, whereas in the previous campaigns (1970, 1978, 1984), the Brewer-Mast measured 12% less tropospheric ozone than the ECC. This result may indicate a change in the sensitivity of the Brewer-Mast to ozone. However, this conclusion cannot be made with certainty as the preflight preparations during campaigns can be different from those used at home, so that it is hard to assess how representative the campaign measurements are. The implications for the trends in tropospheric ozone are discussed below.

Different techniques produce measurements of varying quality at different altitudes, and it is important to know where to trust a particular technique. Ozonesondes operate well in the stratosphere up to altitudes of 25 to 30 km: they currently provide the only record of measurements in the free troposphere that is suitable from trend analysis. Measurements by SAGE are used for analyses of trends down to 15 km. However, as previously mentioned, the ozone trends in the 15 to 20 km range are sensitive to the difference in altitude registration between SAGE I and II and to the stratospheric aerosol loading as the aerosol extinction will be strongest when the occultation technique is used to measure through the aerosol layer.

The retrievals used in the Umkehr and SBUV measurements can both calculate vertical distributions of ozone which are not uniquely determined, with the retrieved ozone amount in one layer depending to some extent on the retrieved amounts in other layers (the size of this effect depends on the vertical resolution used) and on the assumed shape within the layer. The possibility thus exists that a trend in one layer could induce trends in other layers, and for this reason, great care must be taken when calculating trends from Umkehr and SBUV data. Unfortunately, the critical 15 to 20 km altitude range is particularly sensitive to these effects and so we err on the side of caution and do not use SBUV retrieved ozone amounts at pressures greater than 32 mbar (i.e., altitudes below about 24 km) for trend analyses. Similarly, the Umkehr ozone amounts at pressures greater than 62 mbar (altitudes below about 19 km) were not considered suitable for trend analysis at the current time. Recent work does indicate that the trends from Umkehr and ozonesondes are consistent at these altitudes [*Miller et al.*, 1995], but more work is needed to be sure that this agreement is not simply fortuitous.

Ozone Trends

Analysis

In addition to sufficiently stable data sets, the calculation of meaningful ozone trends requires a statistical analysis which produces sensible estimates of the uncertainties in the trends and which therefore can assess the possible influence on the estimated trends of a number of mechanisms which affect ozone. For total ozone an approach has been developed which can now be thought of as standard, namely a time series model which includes terms for the unperturbed seasonal cycle, a number of geophysical influences such as the quasi-biennial oscillation (QBO), and the 11-year solar cycle, autocorrelated noise and a seasonally dependent trend term [e.g., *Reinsel et al.*, 1987, 1994a; *Rowland et al.*, 1988]. A weighted regression is used because ozone levels are more variable in winter months than in summer months. Typically the 10.7 cm radio flux is used, unlagged, to mimic the solar cycle effect, and the 50 mbar tropical wind (an average of Ascension, Balboa, and Singapore) to mimic the QBO with an appropriate latitude dependent time lag. For the long-term Dobson data analyses the trend fitted for each month is a "hockey stick," with a level baseline prior to 1970 and a linear trend thereafter. For series beginning after 1970, including all satellite data, the trend is a simple linear monthly trend. The results presented here for total ozone have been calculated using such a model unless explicitly mentioned to the contrary. It is worth noting that these models cannot always be used to determine trends in the vertical distribution of ozone because of the relatively poor temporal quality of the measurements.

The temporal evolution of total ozone since 1979 has been considered by *Solomon et al.* [1996] who compared the TOMS version 6 data with the total ozone from a two-dimensional photochemical model. The surface area of aerosol used in the model is inferred from satellite observations and so varies with time. The timing of the observed ozone changes is in good agreement with the model calculations, but the observed trends are 50% larger. Two other points are clearly made. First, changes in halogen loading and aerosol loading must be considered jointly for their effect on ozone trends. Second, it is possible that the aerosol induced ozone changes could be confused with the effects of the solar cycle and that the latter may be overestimated by statistical models such as that used here. There should be only a small secondary impact on the calculated ozone trends.

Trends

Total ozone. The trends for 43 individual ground stations from January 1979 to February 1994 are shown in Figure 3 and given in Table 1, together with the trends calculated from the reassessed filter ozonometer data for four large regions of the former USSR [*Bojkov et al.*, 1994]. Overall, there is a clear latitudinal pattern as shown by the zonal averages, although there is substantial scatter in the trends found at individual stations, presumably caused both by real longitudinal variations in trends (largest in December-February) and by remaining errors in the data. Further analysis of the 30 year ground-based total ozone record is presented by *Bojkov et al.* [1995a].

Figure 4 shows the trends calculated from the SBUV(/2) measurements from January 1979 to June 1994 as a function of latitude and time of year. The same basic features are apparent in both data sets, as has been noted previously: the year-round loss in northern midlatitudes (4%/decade) with larger losses occurring in winter/spring (as large as 7%/decade); the small, but statistically insignificant loss in the tropics (1-2%/decade); and the year-round losses in southern midlatitudes (3-6%/decade), with some sign of larger losses in spring. A typical standard error associated with the SBUV(/2) trends is 1%/decade.

The trends calculated for the period 1/79 to 5/91 using measurements from the Dobson network, SBUV(/2) and TOMS (version 6) are shown in Figure 5. The agreement between the trends is typically to within 1-2%/decade. In general, the SBUV(/2) trends are more negative than those from TOMS or the Dobson network, most noticeably in the tropics and in southern midlatitudes. The statistical

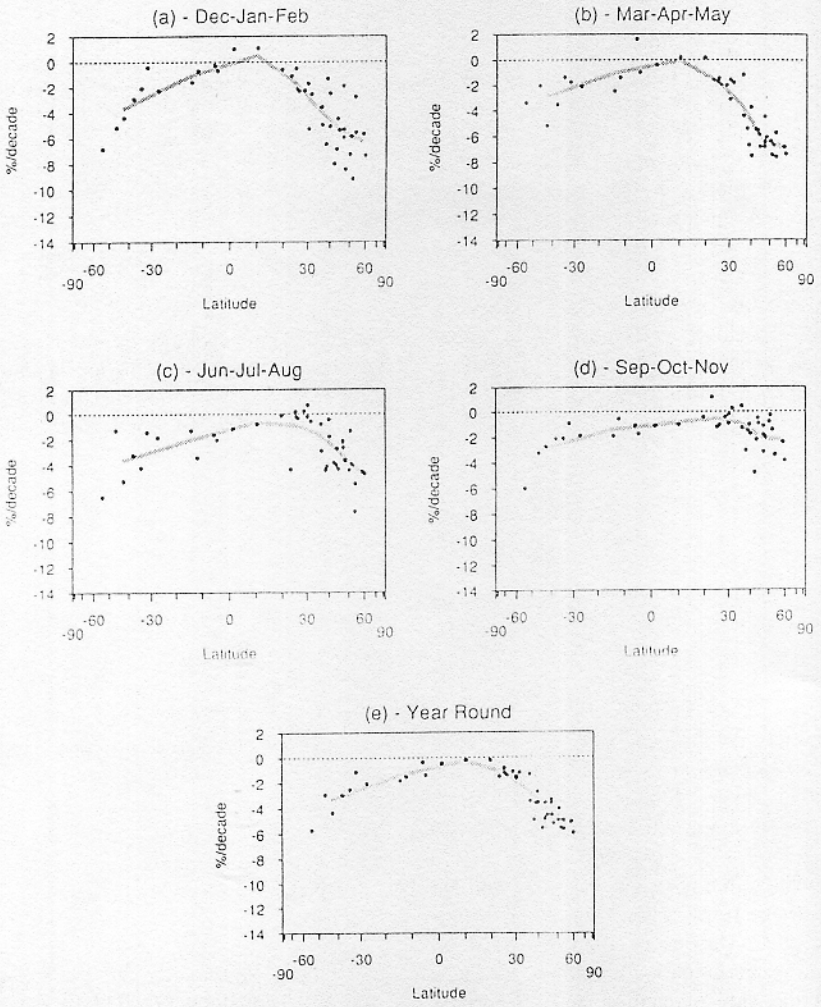

Figure 3. Individual Dobson station seasonal trends in total ozone in percent per decade against latitude, over the period January 1979 through February 1994 (where data are available). The grey curves are the averages of the individual station trends in the following latitudinal zones: 55°-30°S, 30°S-0°, 0°-20°N, 20°-30°N, 30°-40°N, 40°-50°N, and 50°-65°N. The trends and the association uncertainties are given in Table 1.

significance of the trends in the tropics thus depends quite critically on which measurement system is considered the most reliable in this region, a judgement which has not been made to date. However, it may be unrealistic to expect better agreement between three largely independent measuring systems.

The calculated trends have a similar sensitivity to the length of period considered, with changes of one year in the end date of the record causing changes of as much as 2%/decade at 40°-50°N [*Hollandsworth et al.*, 1995] and smaller changes at more southerly latitudes. A longer-term acceleration of the trends is discussed below.

Stolarski et al. [1992] discussed the longitudinal variation in the trends and noted the large differences that exist in winter. They found that the variations at 60°N were marginally statistically significant. *Hood and Zaff* [1995] studied this issue using a simple mechanistic ozone transport model. They concluded that the longitudinal dependence of total ozone trends in January could be explained by decadal changes in the planetary wave behavior in the upper troposphere and lower stratosphere which in turn resulted from decadal climate variability in the troposphere. A similar conclusion was reached by *Randel and Cobb* [1994] who examined the correlation between total ozone and lower stratospheric temperatures (Figure 6).

Randel and Cobb [1994] also investigated the effects of geophysical phenomena such as solar cycle, QBO, and El Nino-Southern Oscillation (ENSO). The 'standard' statistical analysis of the ozone time series included terms to allow for the effect of the solar cycle and the QBO. The ENSO signal in the total ozone record depends strongly on location and time of year and at its largest can be as much as 5% in winter-spring over the northern Pacific but on zonal or other large area means is typically about 1% [*Randel and Cobb*, 1994; *Zerefos et al.*, 1992; 1994].

Stratospheric ozone trends. It is important for several reasons to know the altitudes where the changes in the vertical distribution have occurred. Such knowledge constrains the mechanisms used to explain changes in total ozone; the changes at different altitudes within the profile should balance those observed in total ozone; and the climate impact of ozone changes depends strongly on their altitude. Unfortunately, for the reasons discussed earlier, the overall quality of the available sets of measurements is not so high as

Table 1. Set of 43 Dobson Stations Used for Trend Analyses, With Dates of Usable Data (Although the Earliest Analysis in this Report Begins at January 1964)

				Dec.-Feb.		March-May		June-Aug.		Sept-Nov.		Year		
Station	Latitude	First	Last	est	2se	est	2se	est	2se	est	2se	est	2se	Src
St. Petersburg	60.0 N	68-08	94-02	-7.4	5.5	-7.4	4.2	-4.7	2.7	-3.8	3.1	-6.0	2.3	Sta
Churchill	58.8 N	65-01	93-10	-5.7	4.2	-6.9	3.4	-4.5	2.3	-2.4	3.2	-5.0	1.8	Sta
Edmonton	53.6 N	58-03	94-02	-5.6	4.7	-7.6	3.3	-5.5	2.2	-3.4	3.2	-5.6	1.9	Sta
Goose	53.3 N	62-01	94-02	-2.8	5.4	-5.7	4.4	-7.6	3.0	-3.4	2.8	-4.9	2.4	Sta
Belsk	51.8 N	63-04	93-12	-9.1	5.4	-6.7	4.0	-4.0	2.4	-1.4	3.2	-5.5	2.3	Rev
Uccle	50.8 N	71-07	94-02	-5.9	5.4	-7.4	3.8	-1.3	2.4	-0.3	3.4	-4.0	2.2	WODC
Hradec Kralove	50.2 N	62-03	94-02	-7.3	5.3	-6.4	3.8	-4.4	2.4	-0.8	2.9	-4.9	2.2	WODC
Hohenpeissenberg	47.8 N	68-05	94-02	-8.4	4.7	-6.1	4.6	-3.6	2.6	-2.0	3.1	-5.2	2.4	Sta
Caribou	46.9 N	62-09	94-02	-5.3	4.4	-6.5	2.7	-2.6	2.2	-3.1	3.3	-4.5	1.8	Sta
Arosa	46.8 N	57-07	94-02	-5.9	4.7	-4.5	3.8	-2.2	2.0	-1.1	2.6	-3.6	2.1	Sta
Bismarck	46.8 N	62-12	94-02	-1.9	3.5	-6.8	2.9	-2.1	2.3	-1.8	2.1	-3.3	1.5	Sta
Sestola	44.2 N	76-11	94-02	-5.4	4.7	-6.8	4.0	-4.3	2.2	-0.9	3.0	-4.6	2.0	Rev
Toronto	43.8 N	60-01	94-02	-4.5	3.7	-5.9	2.8	-2.7	1.8	-0.5	3.1	-3.6	1.6	Sta
Sapporo	43.1 N	58-02	94-02	-6.8	3.7	-5.6	3.1	-4.0	2.6	-2.2	2.6	-4.8	1.8	WODC
Vigna Di Valle	42.1 N	57-07	94-02	-8.0	4.3	-5.5	5.1	-3.8	2.4	-4.8	2.7	-5.6	2.4	Rev
Boulder	40.0 N	76-09	94-02	-2.5	3.2	-7.5	3.2	-1.7	1.6	-1.7	2.6	-3.6	1.6	Sta
Shiangher	39.8 N	79-01	93-08	-5.1	3.2	-3.8	3.6	-0.4	2.7	-1.0	2.8	-2.7	1.8	WODC
Lisbon	38.8 N	67-08	94-02	-1.3	3.4	-6.7	2.8	-4.1	1.7	-1.5	2.7	-3.6	1.4	Sta
Wallops Island	37.9 N	57-07	94-02	-6.5	3.5	-5.4	3.5	-4.4	2.2	-3.0	3.3	-4.9	1.9	Sta
Nashville	36.3 N	62-08	94-02	-5.0	3.3	-4.4	3.9	-2.9	2.6	-1.3	3.1	-3.5	1.9	Sta
Tateno	36.1 N	57-07	94-02	-3.6	3.7	-1.2	3.3	-0.8	2.2	0.5	2.3	-1.3	1.7	Sta
Kagoshima	31.6 N	63-02	94-02	-2.6	3.1	-1.8	3.1	-0.6	1.9	0.3	2.0	-1.2	1.6	Sta
Quetta	30.2 N	69-08	93-02	-5.3	4.3	-1.6	4.2	0.7	2.7	-0.2	2.5	-1.6	2.5	Rev
Cairo	30.1 N	74-11	94-02	-1.7	4.0	-3.1	3.0	-0.2	1.6	-0.9	1.6	-1.5	1.7	Sta
New Delhi	28.7 N	75-01	94-02	-2.2	3.3	-2.0	3.2	0.3	2.9	-0.4	1.5	-1.1	1.9	WODC
Naha	26.2 N	74-04	94-02	-2.3	3.0	-2.0	2.9	-0.3	1.7	-1.0	2.0	-1.4	1.5	WODC
Varanasi	25.3 N	75-01	94-02	-2.2	2.4	-1.4	2.5	-0.2	2.5	-1.2	1.9	-1.2	1.5	Rev
Kunming	25.0 N	80-01	94-02	-0.5	2.6	-1.8	3.5	0.2	1.8	-1.2	1.7	-0.8	1.6	Rev
Ahmedabad	23.0 N	59-01	92-12	-1.1	2.7	-1.6	3.4	-4.3	1.7	1.2	2.5	-1.5	1.7	Rev
Mauna Loa	19,5 N	64-01	94-02	-0.6	3.4	0.2	3.1	-0.1	2.3	-0.4	1.9	-0.2	1.8	Sta
Kodaikanal	10.2 N	76-08	94-02	1.1	2.6	0.2	2.6	-0.8	2.8	-1.0	2.9	-0.2	2.1	WODC
Singapore	1.3 N	79-02	93-10	1.0	3.1	-0.4	4.0	-1.1	3.0	-1.1	3.3	-0.4	2.9	Rev
Mahe	4.7 S	75-11	93-10	-0.7	1.8	-1.0	2.4	-2.0	2.5	-1.7	2.3	-1.4	1.6	Rev
Natal	5,8 S	78-12	94-02	-0.3	2.5	1.6	2.0	-1.6	2.4	-1.1	2.4	-0.4	1.6	Rev
Huancayo	12.1 S	64-02	92-12	-0.7	1.7	-1.4	2.0	-3.4	2.8	-0.5	2.1	-1.5	1.5	Rev
Samoa	14.3 S	75-12	94-02	-1.6	1.9	-2.5	1.8	-1.3	3.1	-1.9	2.5	-1.8	1.7	Sta
Brisbane	27.4 S	57-07	93-07	-2.2	1.8	-2.1	1.7	-1.8	3.6	-1.9	2.4	-2.0	1.5	Rev
Perth	31.9 S	69-03	94-02	-0.4	1.4	-1.7	2.0	-1.4	3.4	-0.9	2.0	-1.1	1.3	Rev
Buenos Aires	34.6 S	65-10	94-02	-2.1	1.5	-1.4	2.4	-4.2	3.3	-2.0	3.4	-2.5	1.6	Sta
Aspendale	38.0 S	57-07	93-07	-2.9	1.6	-3.5	1.6	-3.2	2.8	-2.1	2.4	-2.9	1.2	Rev
Hobart	42.8 S	67-07	92-04	-4.4	2.1	-5.2	2.7	-5.2	3.4	-2.7	2.7	-4.3	1.6	Rev
Invercargill	46.4 S	70-07	94-02	-5.2	1.6	-2.0	2.1	-1.2	2.6	-3.2	2.6	-2.9	1.2	Rev
MacQuarie Island	54.5 S	63-03	93-06	-6.8	2.6	-3.4	3.0	-6.5	4.8	-6.0	3.2	-5.7	1.9	Rev

Stations are grouped by the latitude zones used in Figures 3 and 5. Seasonal trend estimates by station are shown for the period January 1979 through February 1994; these are plotted in Figure 3. The columns labeled "2se" give 95% uncertainty limits (two standard errors). The station set is a subset of the 56 stations used by *Reinsel et al.* [1994], with the addition of the record from Lisbon which has since been revised. "Src" column indicated the source of the data used here, with the following codes: WODC, data from World Ozone Data Centre; Sta, data supplied by the station authorities; Rev, revised. For details of the station selection criteria, see chapter 1 in *WMO-UNEP* [1995].

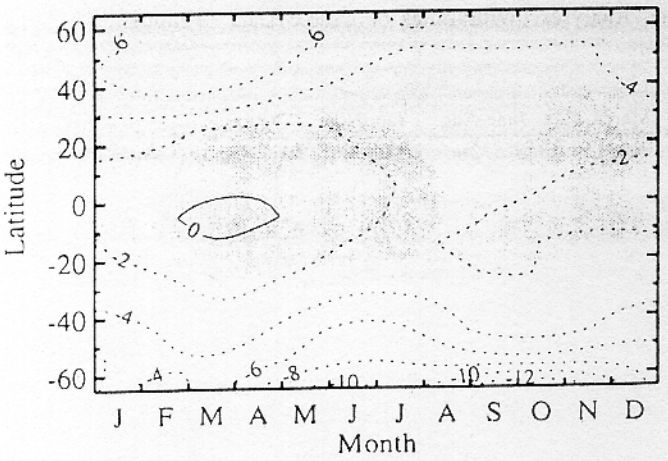

Figure 4. Trend in total ozone in percent per decade as a function of latitude and season based on the SBUV(/2) data through June 1994. The shaded region indicates trends which are not significant at the 2σ level [from *Hollandsworth et al.*, 1995].

that for the set of total ozone measurements, and the uncertainties associated with calculated trends in the vertical ozone distribution are larger. However, a number of conclusions can be drawn with confidence.

The largest ozone loss, in terms of the effect on the column amount, has taken place in the lower stratosphere between about 15 and 25 km. Figure 7 shows the trends (in percent/decade) calculated from SBUV(/2), Umkehr, SAGE I/II, and ozonesondes during the 1980s. Such a comparison is only possible between 30° and 50°N as there are insufficient ozonesonde and Umkehr records elsewhere. It is clear that at these latitudes the quantitative agreement between SAGE and ozonesondes is good at altitudes above 20 km (trends in the range -3 to -5%/decade; -7 ± 4%/decade at 20 km) but is not good within a limited altitude range lower down (at 17 km, SAGE: -20 ± 8%/decade; sondes: -7 ± 3%/decade). The effect of the SAGE adjustments by *Wang et al.* [1996] in the very low stratosphere is not assessed, but at midlatitudes, their SAGE I altitude correction is similar to the one used in the analysis shown in Figure 7.

The long-term ozonesonde records have been thoroughly reviewed by *Logan* [1994], and *Miller et al.* [1995] have

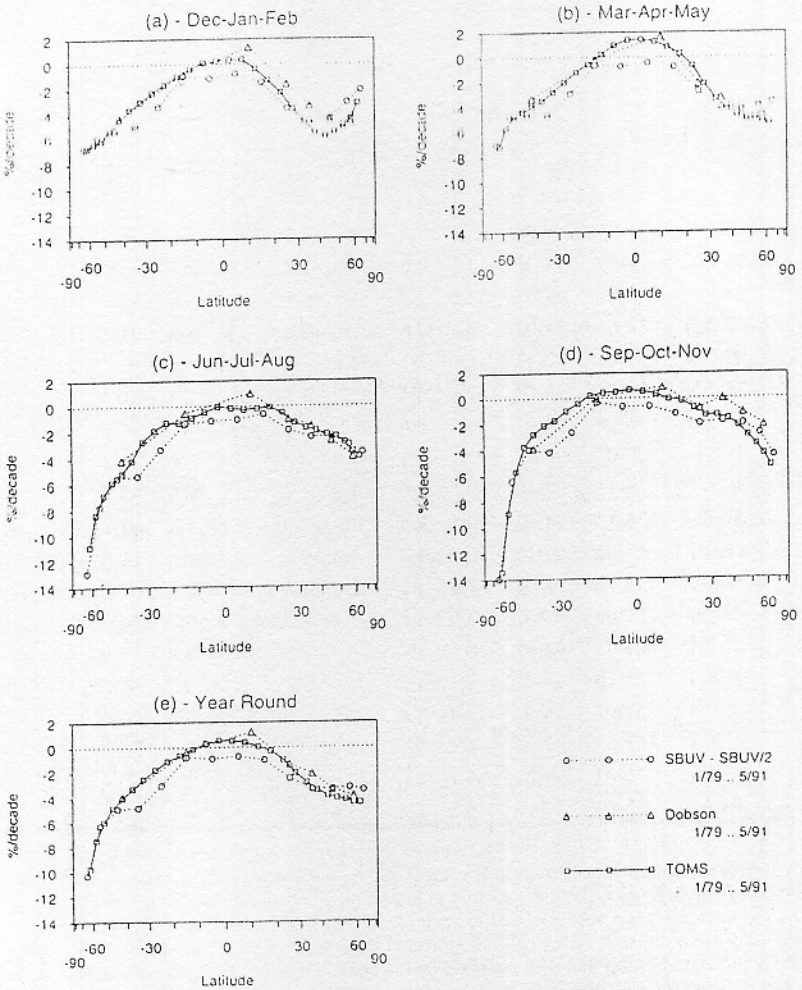

Figure 5. SBUV(/2), Dobson, and TOMS seasonal total ozone trends in percent per decade by latitude from January 1979 to May 1991. Circles show SBUV(/2) trends, triangles show Dobson trends, and squares show TOMS trends. The Dobson trends are averages within latitudinal zones of individual trends at 59 Dobson stations. Typical 95% confidence limits are 1-2%/decade.

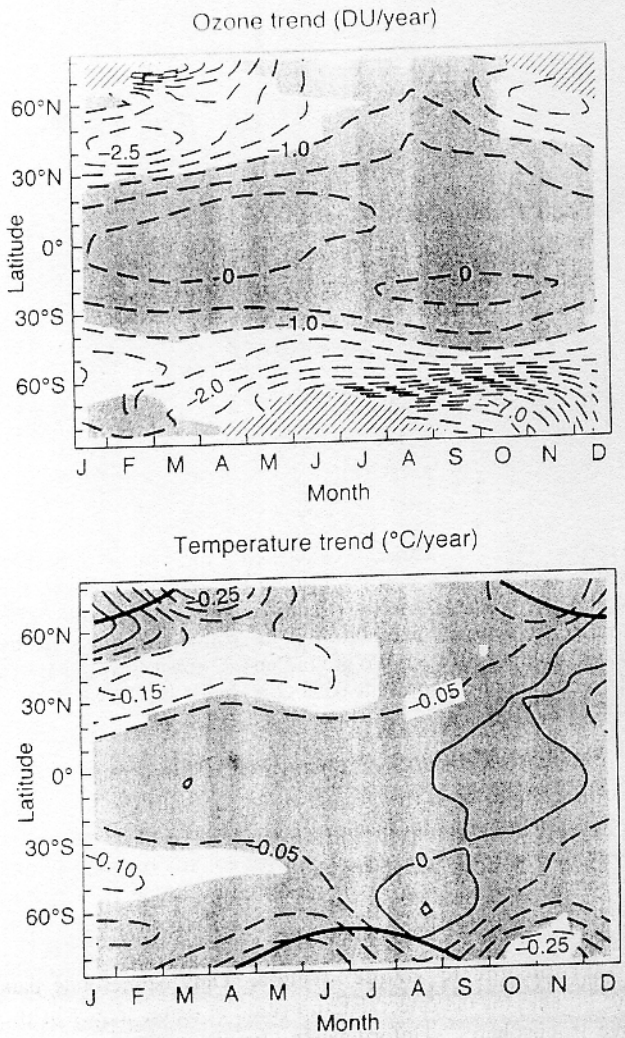

Figure 6. Latitude-longitude diagrams of ozone and temperature trends during January-February for data over 1979-1991. No ozone data are available in the hatched region poleward of 68°N in the top panel [from *Randel and Cobb*, 1994].

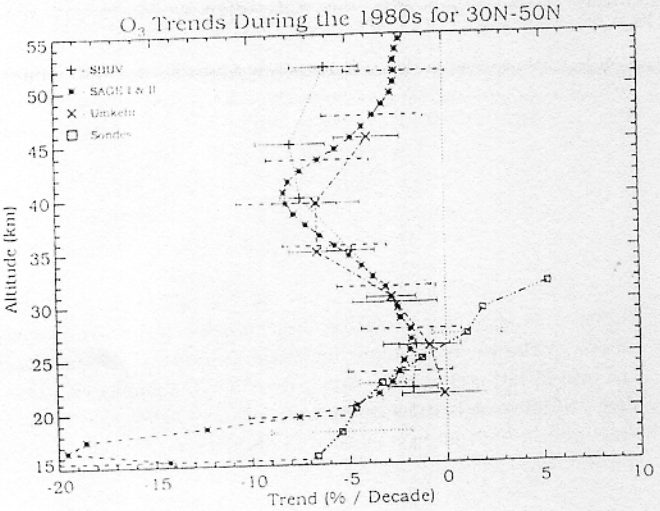

Figure 7. Comparison of trends in the vertical distribution of ozone during the 1980s. Ozonesonde and Umkehr trends are those from *Miller et al.* [1995]; 95% confidence limits are shown.

calculated trends from both ozonesonde and Umkehr data. These studies gave broadly similar results for the ozonesondes in the lower stratosphere. The large natural variability of ozone concentrations, compounded at some stations by low sampling frequency, causes the trend uncertainties to be large. In the northern midlatitudes, *Logan* [1994] found a maximum trend of -8 to -12%/decade near 90 mbar from the early 1970s to 1991. Decreases extend from about 30 mbar down to near the troposphere. Significant ozone loss occurred between 90 and 250 mbar.

Few conclusions about the seasonal nature of the trends are statistically significant. A possible difference exists between the Canadian ozonesonde records where the summer trends are similar to and possibly even greater than the winter trends. At Wallops Island, Virginia, and at the European stations the winter loss is greater than the summer loss. These features are also seen in the total ozone record from 1978 to 1991 observed at these stations [*Logan*, 1994].

The SAGE I/II trends are shown as a function of latitude in Figure 8. They differ in two respects from those reported previously [*McCormick et al.*, 1992]. First, an altitude correction of 300 m has been applied to the SAGE I measurement. Second, the year used to calculate the percentage change is now 1979, not 1988. Below 20 km the effect of both of these changes is to reduce the SAGE I/II trends because ozone changes rapidly with altitude and because the largest losses are observed at these altitudes so that the change in the base value is greatest. Two other factors complicate the SAGE measurement below 20 km: (1) ozone concentrations are smaller than at the maximum, so that the signal is lower; and (2) the amount of aerosol is greater, which attenuates the signal and acts as an additional interference. These are well-recognized difficulties for which allowance is made in the calculation of the ozone amount and which contribute to the size of the uncertainties in SAGE ozone trends in the lower stratosphere.

Between about 30°N and 30°S the SAGE I/II record shows decreases of more than 20%/decade in a region just above the tropopause. In absolute terms this loss, and its impact on the

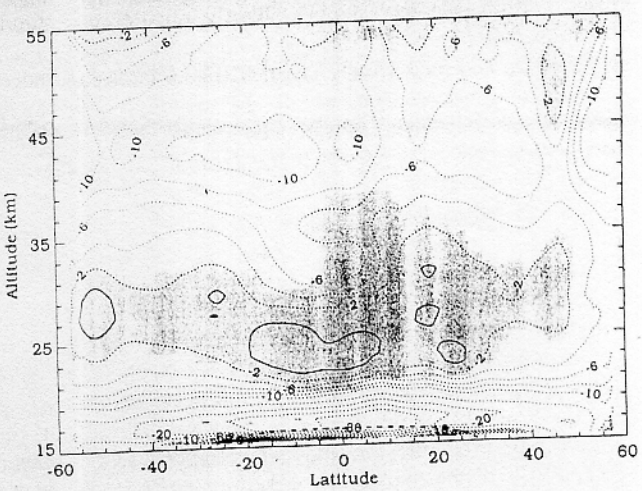

Figure 8. Trends calculated for the Stratospheric Aerosol and Gas Experiment (SAGE) I/II for 1979-1991. Hatched areas indicate trends calculated to be insignificant at the 95% confidence level. The dashed line indicates the mean tropopause. The altitudes of the SAGE I measurements have been adjusted by 300 m at all latitudes.

column amount, is small because there is not much ozone at these altitudes. The height of the peak decrease in ozone is about 17 km and the region of decrease becomes broader away from the equator.

Only Natal (6°S) has an ozonesonde record longer than 10 years near the equator. The trend found by *Logan* [1994] at 70-90 mbar is -10 ± 15%/decade. At Hilo, Hawaii (20°N), ozonesondes from 1982 to 1994 indicate insignificant trends of -12 ± 15%/decade near the tropopause (17-18 km) and -0.7 ± 6%/decade in the lower stratosphere at 20 km [*S. Oltmans*, private communication, 1995]. Trends from both ozonesonde records are smaller than the calculated SAGE I/II tropical trends, but the large uncertainties mean that the trends are not inconsistent. In the southern hemisphere the only long-running station outside Antarctica is at Melbourne, Australia (38°S), where a trend of about -10%/decade is observed in the lower stratosphere, consistent with the SAGE I/II trend at that latitude.

Above 25 km the trends from the different instruments shown in Figure 7 are in good agreement with each other, with the exception of the ozonesondes. At altitudes above 25 km the ozonesonde measurement is less accurate (see above), but some of this difference may also be in the data selection used in the analysis shown [*Miller et al.*, 1995], as Logan does not report a positive trend in this region. The trends calculated from SAGE I/II, SBUV(/2), and Umkehr data at these higher altitudes are in excellent agreement. The ozone destruction here should be dominated by the gas phase processes originally proposed by *Molina and Rowland* [1974], and so these trends are a good test of our understanding of gas phase photochemistry. However, a comparison of the SAGE I/II trends in the tropics (Figure 8) with those found from SBUV(/2) (Figure 9) shows that the agreement at 40 km is worse. While the SAGE I/II trends show little latitudinal structure at this altitude, the SBUV(/2) data show the smallest loss in the tropics. When the SAGE I data are corrected using the latitude correction of *Wang et al.* [1996], there is good agreement between the derived SAGE I/II trends and the SBUV(/2) trends (see Figure 16 in their paper). Both data sets show a slightly smaller midlatitude loss in the northern hemisphere than in the southern hemisphere and increasingly larger losses at higher latitudes.

The seasonal dependence of the trends in the upper stratosphere has been investigated using the SBUV and Umkehr data [*Hood et al.*, 1993; *Deluisi et al.*, 1994; *Reinsel et al.*, 1994b; *Miller et al.*, 1995]. The Umkehr records between 19°N and 54°N do not show a significant seasonal variation in the trend. This is slightly at odds with the analysis of the SBUV measurement which shows that the largest ozone decreases have occurred in winter at high latitudes in both hemispheres, though this difference may not be significant given the problems associated with measurements made at high solar zenith angles.

The SAGE I/II trends (including their adjustments) in the column above about 3 km above the tropopause have been compared with the total ozone trends found from TOMS for 1979-1991 [*Wang et al.*, 1996]. This comparison implicitly assumes little or no change in the ozone amount below 15 km. The largest difference is found in the tropics, but even here the uncertainties are too large to say that the difference is significant. Similar conclusions were reached by *Hood et al.* [1993] who compared the tropical trend from SBUV for the

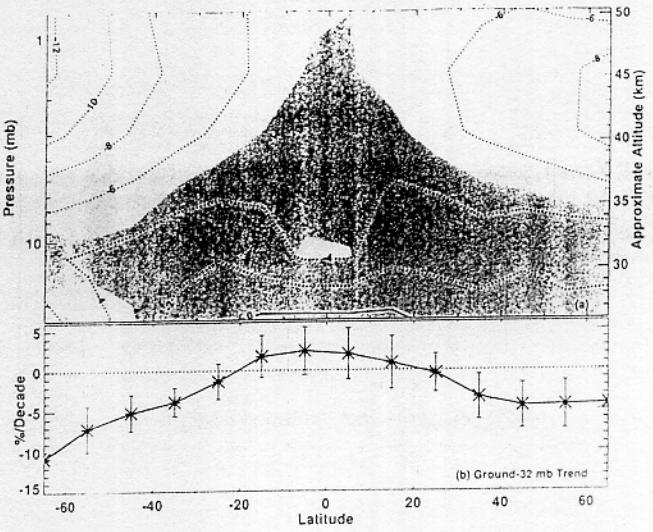

Figure 9. Trends calculated for the combined SBUV/SBUV2 data set for 1/79 to 6/91. Hatched areas in the top panel indicate that the trends are not significant (95% confidence limits). The bottom panel shows the trends in the partial column between the ground and 32 mbar. Error bars in the bottom panel represent 95% confidence levels.

partial column from the ground to 26 km with the SAGE I/II trends reported by *McCormick et al.* [1992] and by *McPeters et al.* [1994] who found that the ozone column between 15 and 55 km (Umkehr layers 3-10) measured by SAGE II decreased relative to that measured by SBUV by 1.1% between 1984 and 1990.

Tropospheric ozone trends. Only ozonesonde data are suitable for the direct determination of ozone trends in the free troposphere. Unfortunately, for the reasons discussed above, the quality of the ozonesonde data in the troposphere is worse than in the stratosphere, partly because the number of high quality, long records is fewer in the troposphere due to changes in sensor with incompletely characterized tropospheric responses. The likelihood of regional differences in trends also confuses attempts to assess the consistency of a limited number of ozonesonde records. Ozone measurements made at the Earth's surface contain some information about free tropospheric ozone levels, but these data must be treated with care in this context because the measured concentrations may not be representative of those in the free troposphere. A coherent, overall view of changes in tropospheric ozone is thus hard to obtain and our current knowledge is based on the tantalizing glimpses described below.

Logan [1994] and *Miller et al.* [1995] have analyzed the global ozonesonde record, paying particular attention to inhomogeneities in the data. A similar study by *London and Liu* [1992] did not account for instrumental changes at some sites. Figure 10 shows the monthly mean ozone values measured in the free troposphere (500 hPa) at 15 ozonesonde stations [*Logan*, 1994]. Two points can be easily seen: the different temporal evolutions at the different stations and the sparseness of some data sets. There is evidence that the upward trend over Europe is smaller since about 1980 than before. The Hohenpeissenberg ozone measurements show no increase since the mid-1980s. The Payerne record shows a

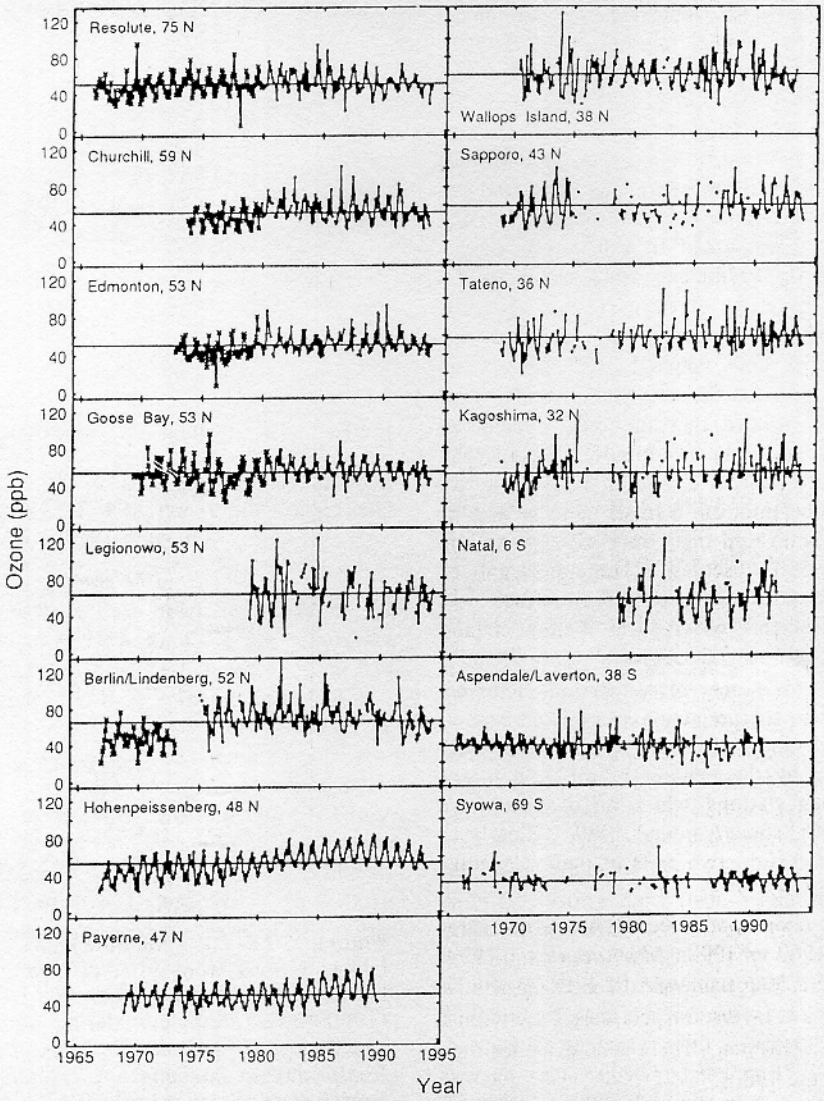

Figure 10. Monthly mean values of ozone at 500 mbar for each ozonesonde station, given in parts per billion. Soundings were included only if the corrections factors met the criteria given by *Logan* [1994]. The change from Brewer-Mast to ECC sondes at the Canadian stations, from Brewer-Mast sondes at Berlin to GDR sondes and then to ECC sondes at Lindenberg, and from GDR to ECC sondes at Legionowo is indicated by the change in symbol type. The year labels mark the start of the year [adapted from *Logan*, 1994].

much smaller increase in the second half of the 1980s than in the first half. (Note that the Payerne data after 1990 are not shown because there were problems with the quality of the ozonesondes).

Some of the trends, particularly those in Europe, might be influenced by changes in SO_2 levels. *De Muer and De Backer* [1994] have corrected the Uccle data set allowing for all known instrumental effects, including SO_2. The ozone trend in the upper troposphere was only slightly reduced (+10 to +15%/decade, 1969-1991) and remained statistically significant. However, below 5 km the trend was reduced and became statistically insignificant, going from around +20%/decade to +10%/decade. *Logan* [1994] argues, using SO_2 emission figures and nearby measurements of surface ozone and SO_2, that measurements made at Hohenpeissenberg, Lindenberg, and possibly other European stations might also be influenced by SO_2 and points out that any such effect would be largest in winter. In polluted areas, local titration of ozone by NO_x can also influence measurements of ozone at low altitude. Neither of these affects should have much influence except in the lower troposphere ($\leq$ 4 km).

Tropospheric ozone over Canada decreased between 1980 and 1993 at about -1 $\pm$0.5%/year [*Tarasick et al.*, 1995]. The positive trend observed at Wallops Island has diminished and from 1980 to 1991 was close to zero [*Logan*, 1994]. Prior to 1980 the situation is more confused. Wallops Island is the only station in North America with a homogeneous record from 1970 to 1991 and a trend of just under +10%/decade was observed.

Many early measurement of ozone over North America were made using Brewer-Mast sondes, while recent measurements have been made exclusively with ECC sondes. A critical factor needed to deduce the long-term tropospheric ozone changes over North America is the ratio of the sensitivities of Brewer-Mast and ECC sondes to tropospheric

ozone. For example, Brewer-Mast ozonesonde measurements were made at Boulder in 1963-1966 [*Dütsch et al.*, 1970], while ECC sondes have been used in the soundings made since 1985 [*Oltmans et al.*, 1989]. *Logan* [1994] compared the Boulder data by multiplying the Brewer-Mast data at 500 and 700 mbar by 1.2, and she concluded that (1) no increase has occurred in the middle or upper troposphere and (2) a 10-15% increase occurred in the lower troposphere caused by local pollution. The factor of 1.2 was based on a reanalysis of the inter-comparisons in 1970, 1978, and 1984 [*Kerr et al.*, 1994, and references therein]. *Bojkov* (1988; private communication, 1994) compared the concurrent measurements made by several hundred ECC sondes at Garmisch-Partenkirchen and Brewer-Mast sondes at Hohenpeissenberg and concluded that the ratio should be between 1.04 and 1.12, depending on altitude. Use of this lower factor would produce a larger change at Boulder in the lower troposphere and would indicate a small increase at 500 mbar. Either way, there is no sign that ozone concentrations over Boulder rose by the 50% observed at Hohenpeissenberg or Payerne since 1967: at most a 10-15% increase has occurred, similar to the increase observed at Wallops Island where ECC sondes have been used throughout.

It is possible that the differences in conversion factor are real and differ according to the prelaunch procedures used at the different sites. If so, no single factor can be used: this explanation is supported by the apparently different jumps seen at the four Canadian stations which all changed from using Brewer-Mast to ECC sondes around 1980. Clearly, a conversion factor is needed if the two parts of these Canadian records are to be combined.

A reanalysis of the ozonesonde records from the three Japanese stations from 1969 to 1990 [*Akimoto et al.*, 1994] found annual trends of 25 ± 5%/decade and 12 ± 3%/decade for the 0 to 2 km and 2 to 5 km layers, respectively. Between 5 and 10 km the trend is 5 ± 6%/year. There is no evidence for a slowing up of trends in the 1980s.

In the tropics, *Logan* [1994] reports that Natal shows an increase between 400 and 700 mbar which is only significant at 600 mbar. The Melbourne record shows a decrease in tropospheric ozone which is just significant between 600 and 800 mbar and is largest in summer.

Measurement of ground level ozone concentrations were made during the last century, mostly by the Schoenbein method [e.g., *Anfossi et al.*, 1991; *Sandroni et al.*, 1992; *Marenco et al.*, 1994]. This technique is subject to interference from wind speed [*Fox*, 1873] and humidity [*Linvill et al.*, 1980], and *Kley et al.* [1988] concluded that these data are only semiquantitative in nature and should not be used for trend estimates. A quantitative method was used continuously from 1876 to 1911 at the Observatoire de Montsouris, Paris [*Albert-Levy*, 1878; *Bojkov et al.*, 1986; *Volz and Kley*, 1988]. The average ozone concentration was around 10 ppbv, about a factor of 3-4 smaller than those found today in many areas of Europe and North America. However, the measurements at Montsouris were made close to the ground and hence are not representative of free tropospheric ozone concentrations during the last century.

Staehelin et al. [1994] compared ground level measurements made by optical and chemical techniques at a number of European locations since the 1930s [*Götz and Volz*, 1951; *Perl*, 1965]. They found that the concentrations

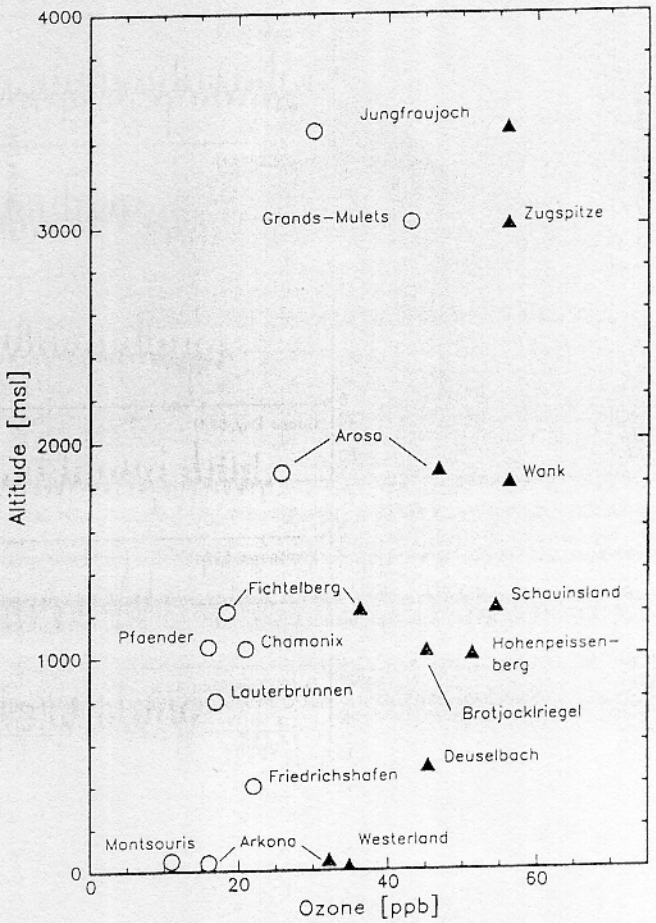

Figure 11. Measurements from surface ozone concentrations from different locations in Europe performed before the end of the 1950s (circles) and in recent years (1990-1991, triangles) during August and September as function of altitude [reprinted from Atmospheric Environment, *Staehelin et al.*, [1994] with kind permission from Elsevier Science Ltd., UK].

in the troposphere over Europe (0-4 km) today seem to be a factor of 2 larger than in the 1930s or 1950s (Figure 11). Because of the variance between the different sites, little can be inferred about a possible increase in tropospheric ozone before 1950. In this context it is interesting to note, however, that neither the data from Montsouris (1876-1911; 40 masl) nor those from Arosa (1950-1956; 1860 masl) show a single day with ozone concentrations above 40 ppbv [*Volz-Thomas*, 1993; *Staehelin et al.*, 1994].

"Modern" ozone measurements, typically using UV absorption, were started in the 1970s at several remote coastal and high altitude sites [*Scheel et al.*, 1990, 1993; *Kley et al.*, 1994; *Oltmans and Levy*, 1994; *Wege et al.*, 1989]. All stations north of about 20°N exhibit a positive trend in ozone that is significant at the 95% confidence level. On the other hand, a statistically significant trend of -7%/decade is observed at the south pole. The trends by and large increase from -7%/decade at 90°S to +0.7%/decade at 70°N. Somewhat anomalous are the large positive trends observed at the high-elevation sites in southern Germany (1-2%/year); these large trends presumably reflect a regional influence [*Volz-Thomas et al.*, 1993]. It must be noted,

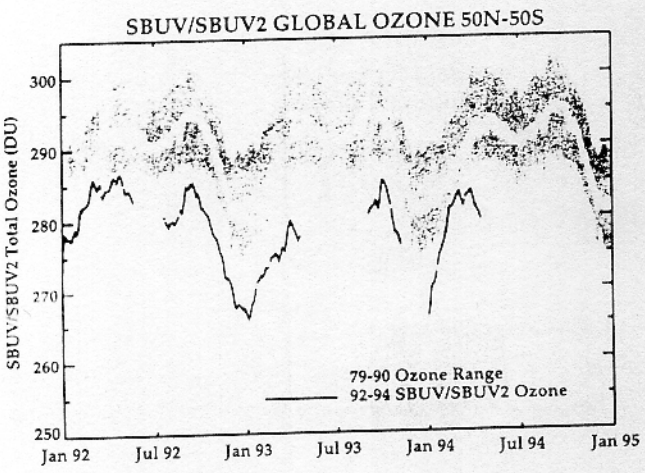

Figure 12. Total ozone (50°N-50°S) measured by SBUV/2 since January 1992 compared with the 1980s range and average from the combined SBUV(/2) record.

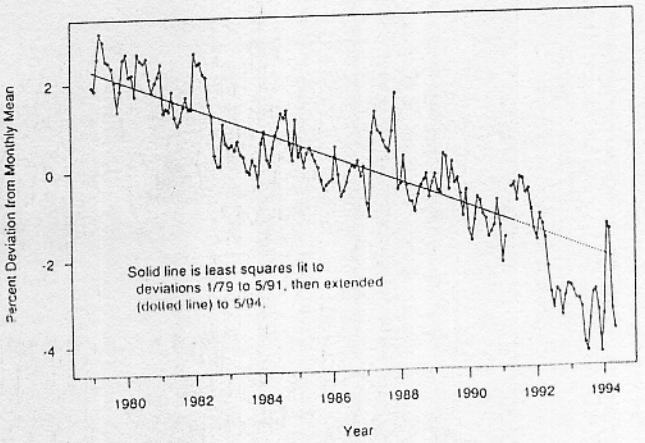

Figure 13. Total ozone (60°N-60°S) from January 1979 to May 1994 measured by SBUV(/2). The annual cycle and the effects of the solar cycle and QBO have been removed. The solid line is a simple least squares fit to the data through May 1991. The dashed line is an extrapolation through May 1994.

however, that the average positive trends observed at the high-altitude sites of the northern hemisphere are largely due to the relatively rapid ozone increase that occurred in the 1970s. If the measurements had been initiated in the 1980s, when the ozone concentrations tended to be at their peak, no significant ozone increase would have been found.

The reasons for the observed changes in tropospheric ozone in the northern hemisphere are not clear. *Logan* [1994] looked at the concurrent changes in the ozone precursor emissions. The trends in the surface emissions of NO_x from Europe and the eastern United States have been similar, so it is not straightforward to explain the large increase in tropospheric ozone over Europe since 1970. *Logan* [1994] also argues that air traffic cannot have been a significant factor as aircraft emissions of NO_x should have roughly followed the use of jet fuel which had increased by 50% since 1980. Variations in stratosphere-troposphere exchange would also affect free tropospheric ozone levels.

Ozone Since 1991

Record low ozone values were observed in 1991-1993. A number of causes have been suggested, which are only briefly discussed here. As noted above, the long-term trends were not greatly affected by these low values, partly because the length of record is sufficiently long for the calculated trends to be relatively independent of a year or two's data and partly because long-term downward trends make record low values more likely to occur. The ozone and temperature changes observed by a number of instruments have been described by *Randel et al.* [1995].

Figure 12 shows the near global (50°N-50°S) daily average ozone amount from 1992 to early 1994, together with the envelope of 1979-1990 observations. Persistent low ozone levels are observed beginning in late 1991, with values completely below the 1979-1990 envelope from March 1992 to January 1994. During 1993, total ozone was about 10-20 DU (3-6%) below the 1980s average. Total ozone values in early 1994 recovered somewhat to the lower end of the range observed in the 1980s.

Figure 13 shows the 60°S-60°N average total ozone from SBUV(/2) after the residuals from a statistical analysis which included terms for the annual cycle, the solar cycle, and the QBO. The most obvious feature in Figure 13 is the long-term decrease in total ozone: the linear trend (-2.9%/decade) fitted to the data from January 1979 to May 1991 (pre-Pinatubo) is shown. The recent (1992-1993) global anomaly is about 2% below the trend line and about 1% less than previous negative anomalies. The 1992-93 anomaly also stands out as the most persistent, spanning nearly 2 years. The only other negative anomaly lasting more than 1 year followed the El Chichon eruption in 1982.

Ground-based measurements of total ozone made at sites with long records show that the anomalies in the northern midlatitudes were the largest since measurements began and that values in early 1993 were about 15% lower than the average values observed before 1970 [*Bojkov et al.*, 1993; *Kerr et al.*, 1993; *Komhyr et al.*, 1994]. The largest ozone losses occurred at higher latitudes in early 1993: deviations were in excess of 60 DU (15% lower than the 1980s mean). Total ozone values over North America in 1994 were in line with the long-term decline but no longer below it [*Hofmann*, 1994; *National Oceanic and Atmospheric Administration (NOAA)*, 1996].

Low total ozone values were seen at high northern latitudes in the 1994/1995 winter [*Bojkov et al.*, 1995b], resulting from the widespread ozone destruction within the Arctic vortex in that winter [*Rex et al.*, 1995; *Braathen et al.*, 1996; *Goutail et al.*, 1996; *Manney et al.*, 1996; *Müller et al.*, 1996] and in the 1995/1996 winter [*NOAA*, 1996]. The aerosol enhancement resulting from the eruption of Mount Pinatubo had largely gone by this time and the ozone loss seems to have been a direct consequence of the very cold temperatures inside the vortex in these two winters.

Figure 14 shows the time evolution at all latitudes (60°S-60°N) of the total ozone deviations found after removal of the trend found for January 1979 to May 1991 (extrapolated to May 1994), the annual cycle and the terms for the solar cycle, and the QBO. The strong regional nature of the deviations is obvious with the largest (6-10%) occurring in northern midlatitudes in January to April 1993. The southern midlatitudes, by contrast, were hardly affected. Large, local

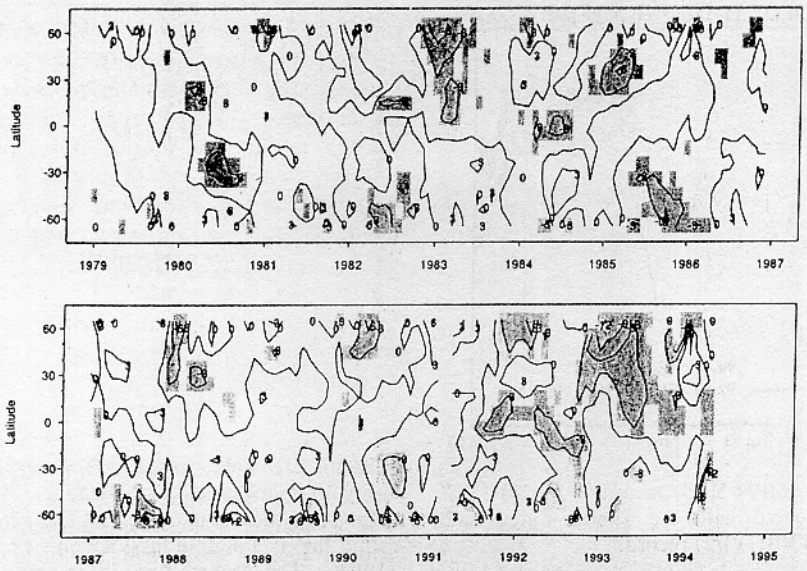

Figure 14. Contour plots of total ozone residuals as a function of latitude and time from the statistical fit to the SBUV(/2) satellite total ozone data from January 1979 to May 1991. The fitted model was extrapolated through May 1994 to calculate the residuals over the extended period January 1979 to May 1994. The total ozone data have the seasonal, trend, solar, and quasi biennial oscillation (QBO) components removed, and the resulting deviations are expressed as percentages of the mean ozone level at the beginning of the series. Contours show constant deviations at intervals of 3%, and the shaded areas indicate negative departures of at least 2%. The 1992-1993 low ozone values are prominent, as well as other periods of very low values in 1982-1983 and 1985.

deviations were seen in the tropics, with negative ozone anomalies of about 15 DU (6%) occurring near the equator from September to November 1991 and in the southern tropics in mid 1992.

Figure 15a shows the ozonesonde measurements at Edmonton made in January-April 1980/1982, 1988/1991, and 1993 [*Kerr et al.*, 1993]. Similar results were found at Resolute, Goose Bay, and Churchill. These indicate that the decrease in early 1993 occurred in the same altitude region as the decline during the 1980s. The standard deviations are ±8 nbar (1980-1992 and 1988-1991 profiles) and ±9 nbar (1993 profiles) where the largest ozone differences are found. The differences between the 1993 and the 1980-82 profiles are statistically significant (2 standard deviations) between 200 and 40 mbar. Ozone levels were depleted by about 25% over approximately 14-23 km (at and below the profile maximum), spatially coincident with the observed aerosol maximum, as shown in Figure 15b [*Hofmann et al.*, 1994a]. Notably, there is substantial ozone increase above the profile maximum (above 25 km) at Boulder, of about 15% of background levels, which is also seen at Hilo, Hawaii [*Hofmann et al.*, 1993].

The eruption of Mount Pinatubo (15°N, 120°E) in June 1991 injected a large amount of sulphur dioxide directly into the lower stratosphere at altitudes as high as 30 km. Within a month or so this sulphur dioxide was oxidized to sulphuric acid which rapidly condensed as aerosol. A large number of observational studies have been published [e.g., *Bluth et al.*, 1992; *Lambert et al.*, 1993; *Read et al.*, 1993; *Trepte et al.*, 1993; *Deshler et al.*, 1993; *Hofmann et al.*, 1994b; *Jäger et al.*, 1995; *McCormick et al.*, 1995], as have a number of simulations [e.g., *Brasseur and Granier*, 1992; *Pitari and Rizi*, 1993; *Rodriguez et al.*, 1994; *Tie et al.*, 1994; *Kinnison et al.*, 1994].

The initial aerosol cloud from Mount Pinatubo dispersed zonally but was confined mostly within the tropics below 30 km for the first several months. By September 1991 the Mount Pinatubo aerosol had moved into the midlatitude southern hemisphere at altitudes between 15 and 30 km. It did not enter into the Antarctic vortex in 1991, unlike the aerosol from Volcán Hudson, which was observed at altitudes of 10-13 km over McMurdo Station, 78°S [*Deshler et al.*, 1992]. In the tropics the Mount Pinatubo plume rose to altitudes of 30 km during December 1991 to March 1992. Strong dispersal from the tropics into the northern middle-high latitudes was observed during the 1991-1992 winter, and enhanced aerosol levels have been detected over 15-25 km in the northern hemisphere since that time. The total mass of the stratospheric aerosol maximized several months after the eruption remained fairly constant until mid 1992, since when it has been declining with an approximate *e*-folding time of 1 year. The total aerosol loading in early 1994 was about 3 to 5 times higher than the background levels observed before the Pinatubo eruption [*Rosen et al.*, 1994; *Thomason et al.*, 1996].

The volcanic aerosol can affect stratospheric ozone through radiative-dynamic effects and through promotion of heterogeneous reactions. The former have been linked with the negative total ozone anomalies of about 15 DU (6%) which occurred near the equator in September-November 1991 [*Schoeberl et al.*, 1993; *Chandra*, 1993], at the same time that the maximum temperature, about 2-3 K at 30-50 mbar, increase was observed [*Labitzke and McCormick*, 1992]. These early tropical ozone anomalies are probably related to enhanced vertical motions induced by the aerosol heating [*Brasseur and Granier*, 1992; *Young et al.*, 1994]. Radiative perturbations to the gas phase photochemistry by the

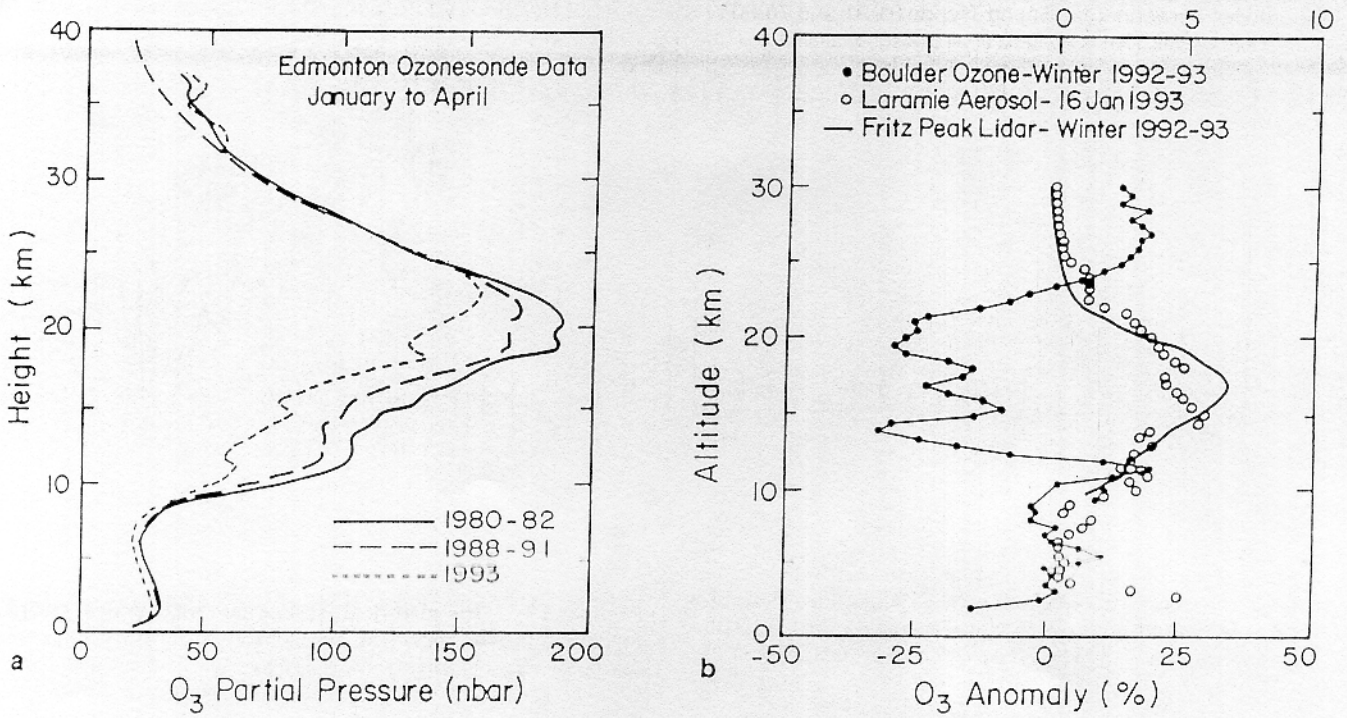

Figure 15. (a) Average ozone profiles found from ozonesonde measurements at Edmonton in spring (January to April) for 1980-1982 (46 sondes), 1988-1991 (42 sondes), and 1993 (13 sondes) [adapted from *Kerr et al.*, 1993]. (b) Percentage differences (bottom axis) in the ozonesonde measurements at Boulder in 1992-1993 relative to 1985-1989. Also shown are the aerosol data from the Fritz Peak lidar (bottom axis, backscatter in 10^8 ST^{-1} m^{-1}) and the University of Wyoming particle counter (top axis, aerosol concentration in cm^{-3}) for winter 1992-93 [adapted from *Hofmann et al.*, 1994a].

initially high concentrations of sulphur dioxide may also have played a part [*Bekki et al.*, 1993].

The Mount Pinatubo aerosol can affect stratospheric chemistry directly by providing a surface on which chemical reactions can occur which lead to a net chemical destruction of ozone. These reactions tend to proceed faster at lower temperatures. Both the 1991/1992 and the 1992/1993 northern winters were cold with later than average final warmings [e.g., *Naujokat et al.*, 1993], and the cold temperatures occurred both within and on the edge of the Arctic vortex, so that there was the opportunity for large areas to be affected.

The other major eruption in the last 15 years was that of El Chichon in early 1982. The stratospheric aerosol surface area following that eruption was approximately half that after the Mount Pinatubo eruption. The total ozone anomalies in 1982/1983 (as compared with 1980, 1981, 1985, 1986 TOMS values) are now thought to have been 3-4% in the 1982/83 winter, smaller than the earlier initial estimates of about 10% [*Stolarski and Krueger*, 1988]. The chemical effects on ozone depends both on the aerosol surface area and on the stratospheric chlorine and bromine loading. On both counts, larger chemical ozone depletion would be expected to have occurred after Mount Pinatubo than after El Chichon. This coupling of aerosol surface area and halogen loading could well be responsible for much of the variation about the long-term trends in ozone observed at midlatitudes since 1979 [*Solomon et al.*, 1996].

Natural variations in ozone are induced by meteorological phenomena such as the El Nino-Southern Oscillation, in addition to the QBO [e.g., *Zerefos*, 1983; *Bojkov*, 1987; *Komhyr et al.*, 1991; *Zerefos et al.*, 1992]. Thus the observed ozone anomalies since 1991 will have been affected to some degree by the prolonged El Nino event which lasted throughout 1992/1993. The amplitude of the El Nino effect in total ozone is 2-6%, but such anomalies are highly localized. While ENSO effects for zonal or large area means were about 1%, ozone in specific areas may have been reduced by an additional 2-3% in 1992-1993 [*Zerefos et al.*, 1992, 1994; *Shiotani*, 1992; *Randel and Cobb*, 1994]. Individual events also strongly affected total ozone on a regional basis: one clear example was the persistent blocking anticyclone in the Northeast Atlantic from December 1991 to February 1992 [*Farman et al.*, 1994]. It is unclear to what extent these phenomena are related and which are the important cause-effect relationships. However, it does appear that a strengthening of polar vortex tends to occur in the northern winters following volcanic eruptions [*Labitzke and van Loon*, 1989; *Kodera*, 1994].

Acceleration of Trends

One obvious question is whether the trends have changed with time. Stratospheric levels of chlorine have increased by a factor of 5-6 in the last 30 years. From 1970 to 1980, total chlorine in the stratosphere is estimated to have increased from 800 parts per trillion by volume (pptv) to 1800 pptv, while by 1990, it had reached 3200 pptv. Bromine levels have also risen. This nonlinear increase, coupled with the non-linear dependence of ozone loss rates on the Cl/Br

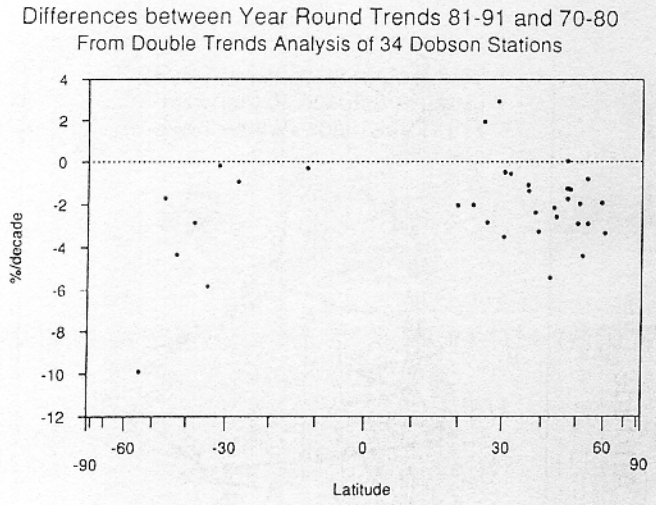

Figure 16. Differences between the trends calculated for 1981-1991 and 1970-1980 at 34 Dobson stations from the analysis using the 'double-jointed hockey stick' model. The average difference (in %/decade with 95% confidence limits) for the 24 stations north of 25°N are annual, -1.8 (0.7); DJF, -2.0 (1.5); MAM, -2.8 (1.1); JJA, -1.9 (1.5); SON, -0.4 (1.2).

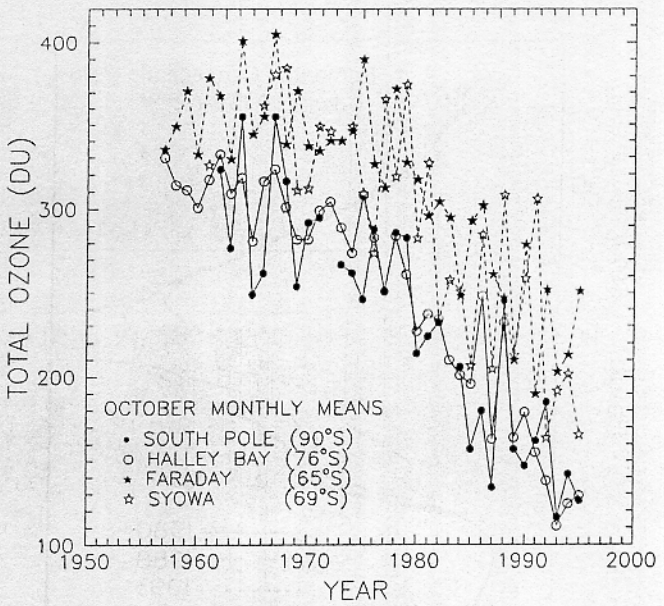

Figure 17. The historical springtime total ozone record for Antarctica as measured by Dobson spectrophotometers during October at Halley Bay, Syowa, and Faraday and from October 15-31 at Amundsen Scott (data courtesy J. Shanklin, T. Ito, and D. Hofmann).

loading (crudely, Cl to the power of 1.7) should have caused an acceleration in the total ozone trends, if indeed they are driven by halogen chemistry. The existence of such an acceleration was hinted at in *WMO* [1992a] where the Dobson trends in the 1979-91 period tended to be larger (more negative) than trends calculated over the longer period 1970-91.

To test the reality and significance of this tendency, a statistical model was used consisting of a "double-jointed hockey stick" with a level base period from 1964 to 1970, a trend beginning in January 1970 and a possibly different trend from January 1981 through December 1991. The date of the trend change was chosen for convenience to divide the 22-year period 1970-1991 into two equal 11-year segments. This model was fitted to 34 Dobson stations whose records began in January 1975. The differences between the annually averaged trends for 1981-1991 and 1970-1980 are shown in Figure 16.

An acceleration can be seen in the annual trends in northern middle to high latitudes where there are 24 Dobson records. Seasonally, the largest trend acceleration appears in spring, followed by those in winter and summer. All these trend accelerations are statistically significant; the only ones which are not are in autumn. Insufficient data exist to test for similar accelerations in the trends found at southern midlatitudes or in the vertical distribution of ozone.

Antarctic Ozone

Total ozone records obtained with Dobson spectrophotometers with traceable calibrations are available for four Antarctic bases: Halley (76°S, formerly Halley Bay) and Faraday (65°S, formerly Argentine Islands) starting in 1957 [*Farman et al.*, 1985; *Jones and Shanklin*, 1995]; Amundsen-Scott (90°S) starting in 1962; and Syowa (69°S) since 1966, although measurements had been first obtained in 1961. Figure 17 shows the October monthly means for these four stations. (Note that for Amundsen-Scott the average is for October 15-31 since inadequate sunlight precludes accurate total ozone measurements with a Dobson instrument before about October 12.)

The two most southern stations (Halley and Amundsen-Scott) show similar long-term total ozone declines in October. The decline in ozone above these stations began in the late 1960s and accelerated around 1980. In 1993, record low values (about 116 DU) were recorded at Halley and Amundsen-Scott. Similarly low values were observed at Halley in 1994 and 1995 (J. Shanklin and A.E. Jones, personal communication, 1995). The decline in total ozone at Faraday and Syowa in October was more subtle, if existent at all, prior to 1980. Again, the major decline occurred between 1980 and 1985, with an apparent stabilization thereafter with total ozone values of about 240-260 DU. While total ozone values have clearly been lower in the 1990s, it is unclear whether an acceleration driven by halogen chemistry has continued, as both chemical and dynamical factors may have contributed to the recent low values. Unusually low mean values of about 160 DU were observed at Syowa in October 1992 and 1995 but were not seen at Faraday.

Figures 3-5 all show significant negative trends outside the polar vortex in the southern hemisphere. These year-round losses must be at least partly caused by the transport of ozone-depleted air out of the Antarctic ozone hole into midlatitudes following vortex breakdown, with the lower ozone values persisting into following years [*Sze et al.*, 1989; *Prather et al.*, 1990; *Mahlman et al.*, 1994]. For instance, the general circulation model simulation of Mahlman *et al.* [1989] shows persistent column ozone depletions of 2-3% over southern hemisphere midlatitudes due to this mechanism. While there are many uncertainties connected with transport in and out of the vortex which limit

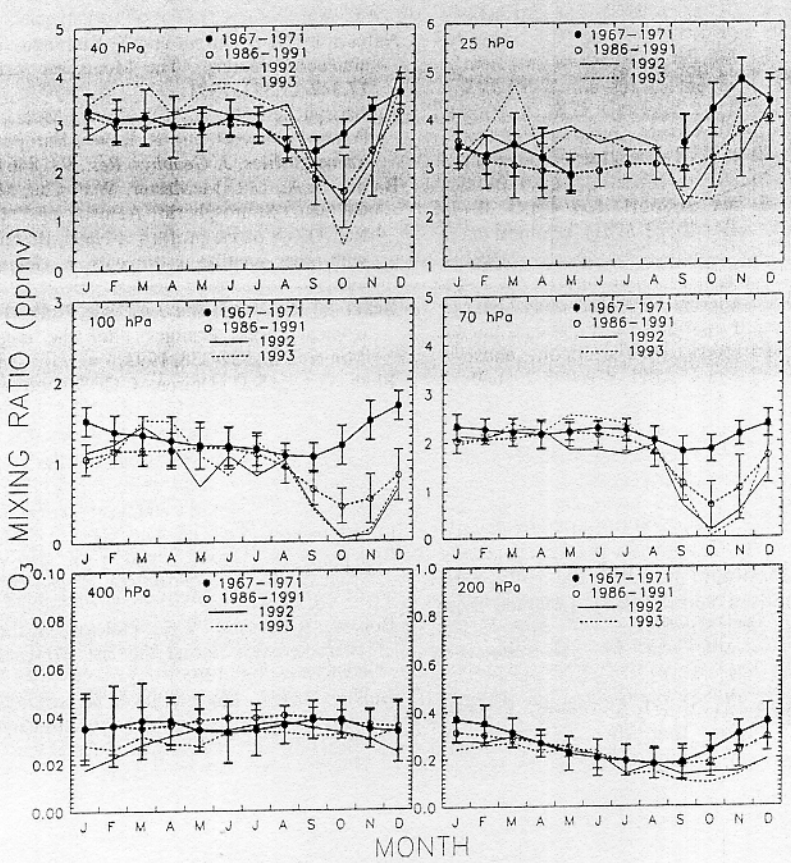

Figure 18. Comparison of smoothed monthly average ozone mixing ratios at six pressure levels above Amundsen Scott for the 1967-1971 period (solid circles and solid lines), the 1986-1991 period (open circles and dashed lines), and for 1992 and 1993 (straight and dashed lines, respectively). The error bars represent ±1 standard deviations [adapted from *Oltmans et al.*, 1994].

the confidence that can be put in such estimates, vortex dilution must be considered in any explanation of the midlatitude trends in the southern hemisphere.

The earliest ozone vertical profiles showing the rapid ozone hole onset were obtained at Syowa in 1983 [*Chubachi*, 1984]. The most extensive set of ozone profile data for trend studies have been obtained at Amundsen-Scott [*Oltmans et al.*, 1994]. This data set comprises roughly 500 profiles measured between 1986 and 1993 and a series of about 85 profiles made between 1967 and 1971. Winter data for the earlier period do not extend to so high an altitude because rubber balloons were used. Figure 18 shows a comparison of smoothed monthly average ozone mixing ratio values for these two periods at six pressure levels between 400 hPa (6.5 km) and 25 hPa (22.5 km). The major springtime ozone difference between the 1967-1971 and the 1986-1991 periods is the depletion in the 14 to 22 km altitude range. The 1967-1971 data indicate a weak minimum in the spring in the 40 to 100 hPa (14-19 km) region. This feature might be a result of ozone loss related to considerably lower stratospheric chlorine levels, consistent with the weak downward trend in total ozone at Amundsen-Scott in the 1960s.

On October 12, 1993, total ozone at the Amundsen-Scott station fell to a new low of 91 DU, well below the previous low of 105 DU measured there in October 1992 [*Hofmann et al.*, 1994b]. Sub-100 DU readings were observed on four occasions and readings in the 90-105 DU range were measured on eight consecutive soundings from September 25 to October 18, 1993. Total ozone in the vortex was slightly higher in 1994 than in 1993, and the lowest measured value at Amundsen-Scot was 102 DU on 5 October [*Hofmann et al.*, 1995].

In Figure 19 the average of four ozone profiles before depletion began in August 1993 is compared with the profiles at the time of minimum ozone in 1992 and 1993 [*Hofmann et al.*, 1994b]. Total destruction (>99%) of ozone was observed from 14 to 19 km in 1993, a 1 km upward extension of the zero ozone region from the previously most severe year, 1992. Unusually cold temperatures in the 20 km region are believed to be the main cause of lower than normal ozone in the 18 to 23 km range. These lower temperatures prolong the presence of polar stratospheric clouds (PSCs), in particular, nitric acid trihydrate (NAT), thought to be the dominant component of PSCs. This tends to enhance the production and lifetime of reactive chlorine and concomitant ozone depletion at the upper boundary of the ozone hole because chlorine in this region is not totally activated in years with normal temperatures. Temperatures at 20 km in September 1993 were similar to those of 1987 and 1989, other very cold years at this altitude. Cold sulphate aerosol from Mount Pinatubo, present at altitudes between 10 and 16 km, probably contributed to the low ozone through heterogeneous conversion of chlorine species.

Since 1991, springtime ozone depletion over Amundsen-Scott has worsened in the 12 to 16 km region with total ozone destruction at 15-16 km in 1992 and 1993. Similar observations were made in 1992 at McMurdo, 78°S [*Johnson et al.*, 1994], Syowa, 69°S [T. Ito, private communication,

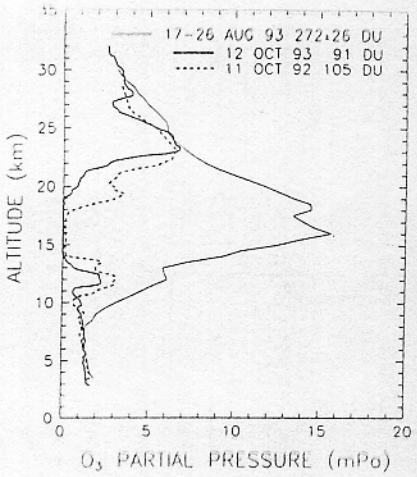

Figure 19. Comparison of the predepletion ozone profile (average of four soundings) in 1993 with the profile observed when total ozone reached a minimum in 1992 and 1993. All measurements made at Amundsen Scott (90°S) [adapted from *Hofmann et al.*, 1994b].

1994] and Georg Forster bases (71°S) [H. Gernandt, private communication, 1994], indicating that this depletion at lower altitudes was widespread. In addition, the 1993 ozone loss was very severe in the 18 to 22 km region, effectively extending the ozone depletion region upward by about 1-2 km (Figure 19). This occurred in spite of ozone being considerably higher than normal during the preceding winter. Complete ozone destruction from 14 to 19 km was peculiar to 1993, and combined with lower than normal ozone at 20-22 km, resulted in the record low total ozone recorded in early October 1993. Ozone recovered in the 12 to 16 km region in 1994 and 1995, probably related to the decay of the Pinatubo aerosol in this altitude range [*Hofmann et al.*, 1995; *NOAA*, 1995].

Total ozone amounts over Halley Bay in January declined at a rate of -1.05 ± 1.13 DU/year between 1976 and 1991, significant at the 90% confidence level [*Jones and Shanklin*, 1995]. This change is qualitatively consistent with the decrease in ozone mixing ratio at 70-200 mbar between 1967-1971 and 1986-1991 at Amundsen-Scott [*Oltmans et al.*, 1994, Fi gure 18]. A slightly smaller decrease is seen in both data sets in February. The magnitude of these changes are similar to those observed at southern midlatitudes. At all altitudes, ozone values from March to August are similar (to within about 10%) in the two periods.

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